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FLAMMABILITY OF HERBICIDE-TREATED GUAVA FOLIAGE

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Fire is one of the most economical and effective means of clearing land. Tropical forests are difficult to burn, due to the adverse environment, rapid decomposition of dead fuel, and high moisture content of the vegetation. Herbicide treatments to kill the trees and provide a more flammable fuel continuum have been suggested. Such treatment will lower the moisture content of the leaves, add to the surface fuels if abscission occurs, and possibly change the chemical composition of the plant material. We have determined some of the chemical changes and changes in flammability of guava leaves (*Psidium guajava* L.) treated with 2,4-D and 2,4,5-T in Puerto Rico.

The major components of natural fuel are cellulose, usually amounting to 40-45 percent by weight, lignin, 30 percent, and hemicelluloses, 25 percent. Lignin does not undergo pyrolysis below 400° C. Above this temperature the reaction is quite slow⁽⁶⁾.¹ Therefore, lignin is probably not very important from a pyrolytic standpoint although it contributes to the glowing reaction. Cellulose makes up approximately 65 percent of the lignin-free fuel, and its pyrolytic mechanisms should have great influence on the way the fuel burns.

The pyrolysis of cellulose can be represented as taking place along two pathways (4). The low temperature pathway leads to CO, CO₂, H₂O, char, and the glowing reaction. The high-temperature pathway leads to about 30 volatiles and the flaming reaction (5). Treatment of cellulose with inorganic contaminants favors the low temperature pathway and a reduction in flammable volatile production² (2, 3). Therefore, inorganic compositional changes in natural fuels could affect pyrolytic and combustion characteristics.

In addition to the above-mentioned pyrolytic compounds, nonpyrolytic compounds also exist in natural fuels. These include terpenes, resins, oils, and waxes; they can be quantified by extractive content. The heat content of these extractives is about 8,000 cal./g. as compared to the fuel, which has approximately 4,400 cal./g. The majority of these compounds volatilize at temperatures considerably lower than 200° C. Variations in extractives should lead to variations in rate of energy release during burning and possibly to changes in rate of spread.

We measured the ash content, ether extractives, and high heat content of treated and untreated guava leaves. The fuels were then subjected to thermogravimetric analysis (TGA), differential thermal analysis (DTA), and small-scale burning tests. This presents the results of these tests.

Methods

The guava was sprayed with a mixture of 12.5 lbs. acid equivalent of 2,4-D and 12.8 lbs. acid equivalent of 2,4,5-T per acre. This was applied as 3 gal. herbicide plus 7 gal. diesel oil per acre. Samples of treated dead leaves, untreated dead leaves, and living foliage (designated in this paper "treated," "dead," and "green," respectively) were collected in Puerto Rico, air-dried, and shipped to the Northern Forest Fire Laboratory, Missoula, Montana.

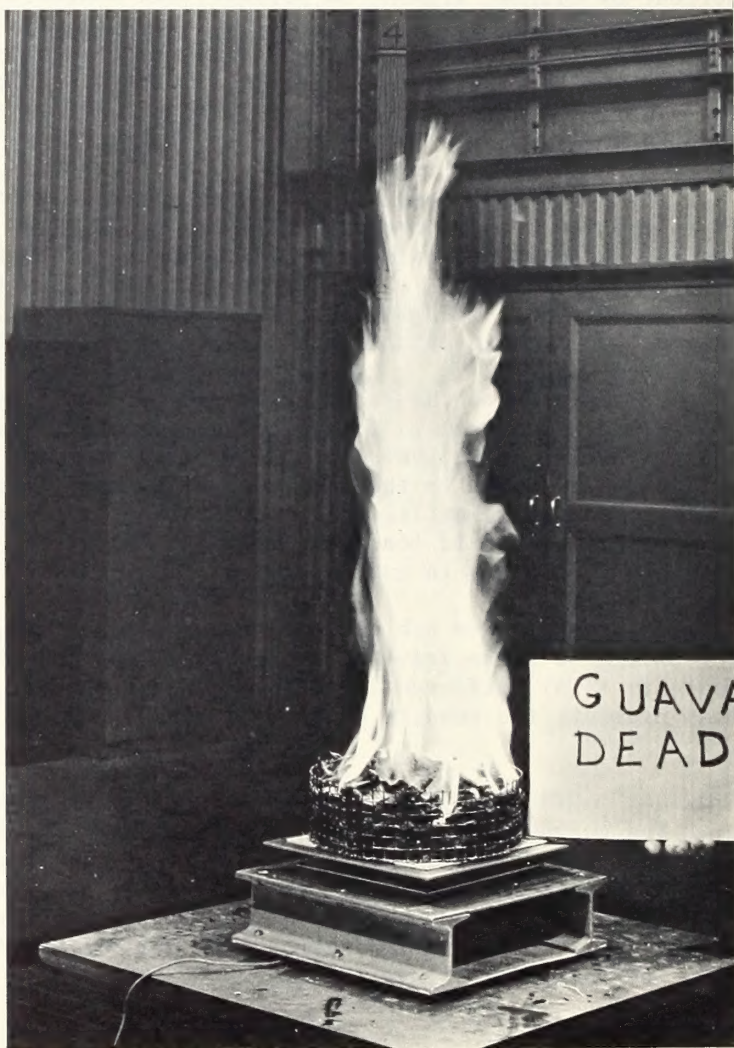
¹ Numbers in parentheses refer to Literature Cited.

² Shafizadeh, F. Pyrolysis and combustion of cellulosic materials. *Advances in Carbohydrate Chemistry* 23: 419-474, 1969. (In press.)

Subsamples were taken, ground to 40 mesh, and used for analysis. Ash content, diethyl ether extractives, and high heat content were determined using standard procedures.³ Three replications of DTA and TGA were performed on a DuPont Model 900 thermal analyzer. The N₂ was 99.98-percent pure by volume. The TGA was run on 10-mg. samples in air or N₂ at 100 cc./min. with a heating rate of 15° C./min. The DTA was run on approximately 5-mg. samples in an N₂ atmosphere, with flushing at 1 liter/min. and heating at 15° C./min., using SiO₂ for reference.

A 60-g. sample (dry weight) of the whole leaves was burned in 0.5-sq.ft. circular fuel beds under controlled conditions. The combustion facilities have been described previously (1). The dry-bulb temperature was 85° F. and the relative humidity 22 percent. The bed was burned by igniting 1 ml. of acetone placed in the center of the fuel. Weight loss was recorded over time with a small weighing platform connected to a 10-lb.-capacity Statham load cell. The output was fed through a voltage divider and into a Bausch and Lomb millivolt recorder (fig. 1).

Figure 1.--Small burning test in controlled environment using a 0.5-sq. ft. circular fuel bed.



³American Society for Testing Materials. D1108-56--Ether solubility of wood; D1102-56--Method of test for ash in wood; D2015-66--Method of test for gross calorific value of solid fuel by the adiabatic bomb calorimeter. ASTM Standards.

Results

The results of the chemical analysis are presented in table 1. The treated fuel was lowest in ether extractives, highest in ash content, and lowest in heat content. The values for ash content of the dead fuel fell between the treated and green. The dead fuel was highest in extractives and heat content.

The TGA and DTA indirectly showed the treated fuel to be less flammable. The cellulose endotherm ($325^{\circ}\text{C}.$) and exotherm ($360^{\circ}\text{C}.$) on the DTA were of the lowest magnitude for the treated fuel; the endotherm occurring at $215^{\circ}\text{--}220^{\circ}\text{C}.$ and the exotherm occurring at $280^{\circ}\text{C}.$ were also the smallest for the treated fuel (fig. 2).

The TGA in N_2 (fig. 3) showed consistent differences between the three fuels. The treated fuel resulted in the highest residue at $450^{\circ}\text{C}.$, the lowest maximum weight loss rate, and the smallest weight loss from 200° to $375^{\circ}\text{C}.$ The TGA in air also showed the lowest maximum weight loss rate (fig. 4) for the treated leaves. The dead fuel underwent ignition at about $350^{\circ}\text{C}.$, but the treated fuel did not ignite until after $440^{\circ}\text{C}.$ However, no ignition tests were performed to check these phenomena.

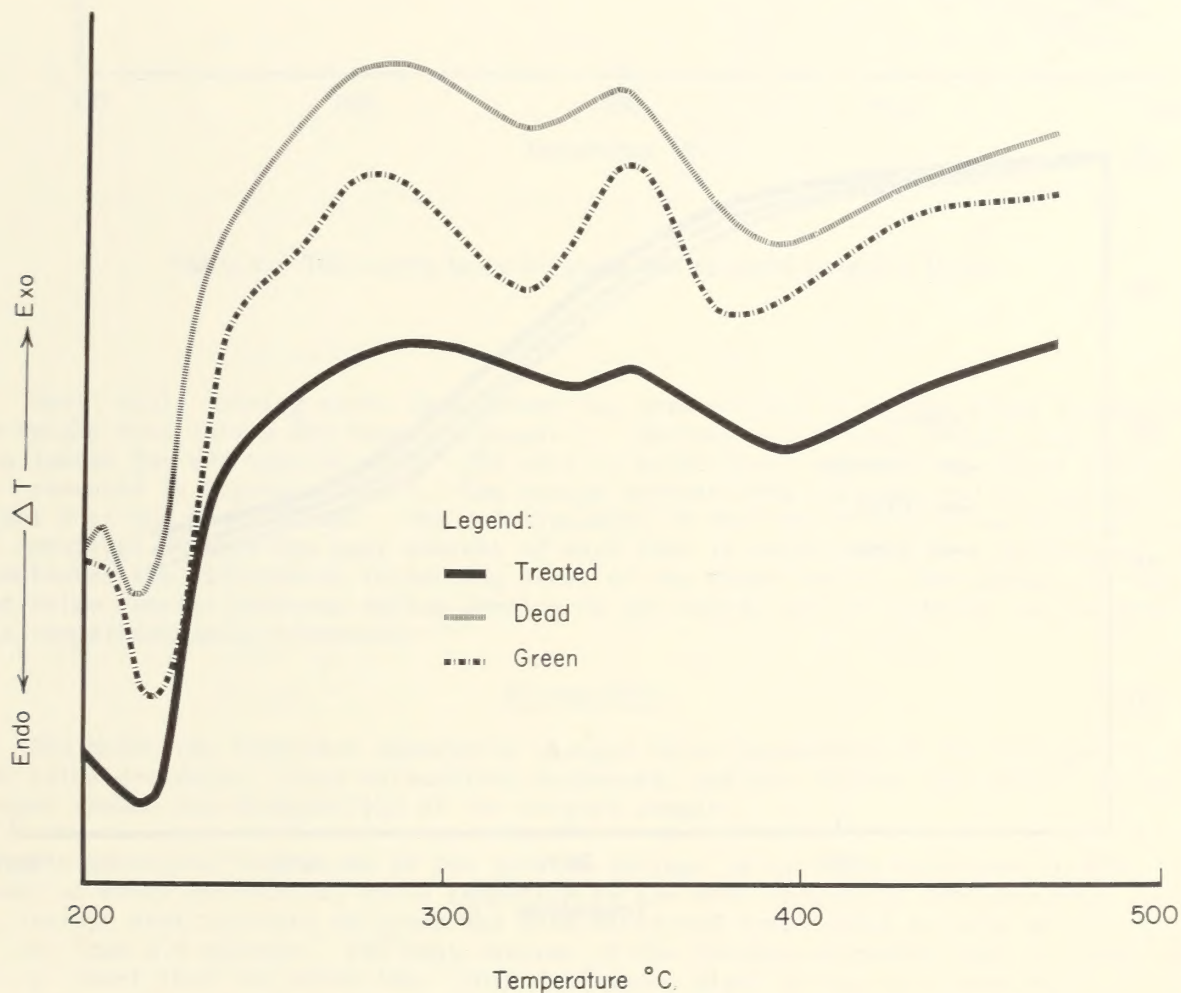


Figure 2.--Results of DTA for guava leaves showing relative magnitude of changes due to treatment. Ordinate zero position is displaced for curve separation.

Table 1.--Analysis of guava foliage

Item	Treated	Dead	Green
Ash content (percent dry weight)	7.79	6.24	6.08
Ether extractives (percent dry weight)	7.60	9.22	8.65
Heat content (cal./g.)	4,495	4,656	4,582
Extracted fuel heat content (cal./g.)	4,200	4,389	4,345
Ashless residue at 450° C. (TGA-N ₂) (percent)	37.2	35.8	34.4
Weight-loss rate--max. (TGA-N ₂) (percent)	0.38	10.42	0.40
Weight loss 175°-350° (TGA-N ₂) (percent)	42	44	46
Weight-loss rate--max. during burning (percent)	1.55	2.00	1.80

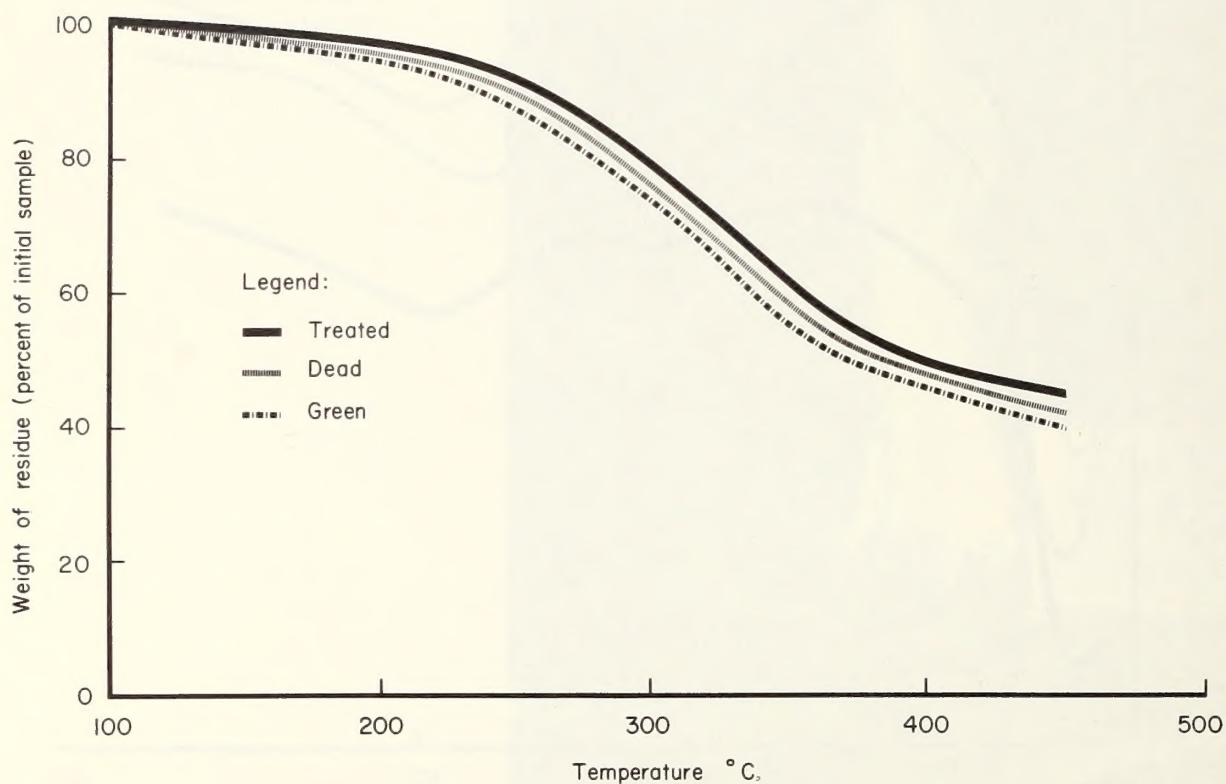


Figure 3.--Results of TGA for 10-mg. samples in N₂ show the effect of fuel treatment. Most rapid weight loss and lowest residue may indicate highest flammability.

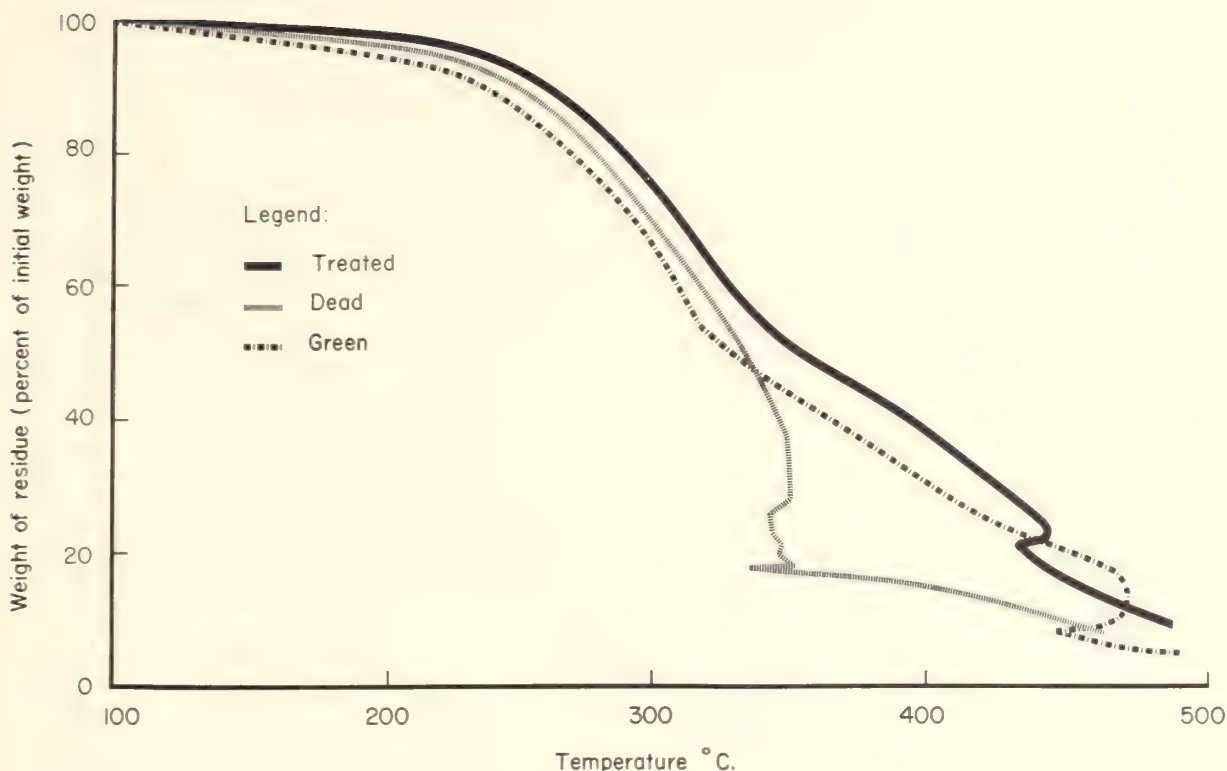


Figure 4.--TGA curves in air for guava with an initial sample of 10 mg.

Small-scale burning tests also showed the treated fuel to be the least flammable. The weight-loss curves are shown in figure 5. Maximum and average weight-loss rates were lowest for the treated fuel. The rate of weight loss and rate of energy release are presented in figures 6 and 7. The energy-release rate was computed by multiplying weight loss and heat content. The relationships of the curves in the two figures are not identical because the heat content of each fuel is different. This difference accentuates the differences in burning rates of the three fuels. The assumption that heat value remains constant during burning is not valid, but it probably can be used in this comparison among treatments.

Discussion

The herbicide treatment apparently changed three parameters of the foliage: the heat value decreased, ether extractives decreased, and ash content increased. These changes reduce the flammability of the treated sample.

The decreased heat value of the treated foliage is due to a reduction in the amount of ether extractives and a reduction in the heat content of the extracted fuel. The average heat contents of green and dead extracted fuel differ by only 44 cal./g., or less than 0.6 percent. The heat content of the treated extracted fuel is about 150 cal./g. lower than the other two. This difference might be due to a more rapid decomposition of the treated foliage, with accompanying reduction in heat content level. The mass change associated with decomposition would also help to account for the high ash content of the treated sample.

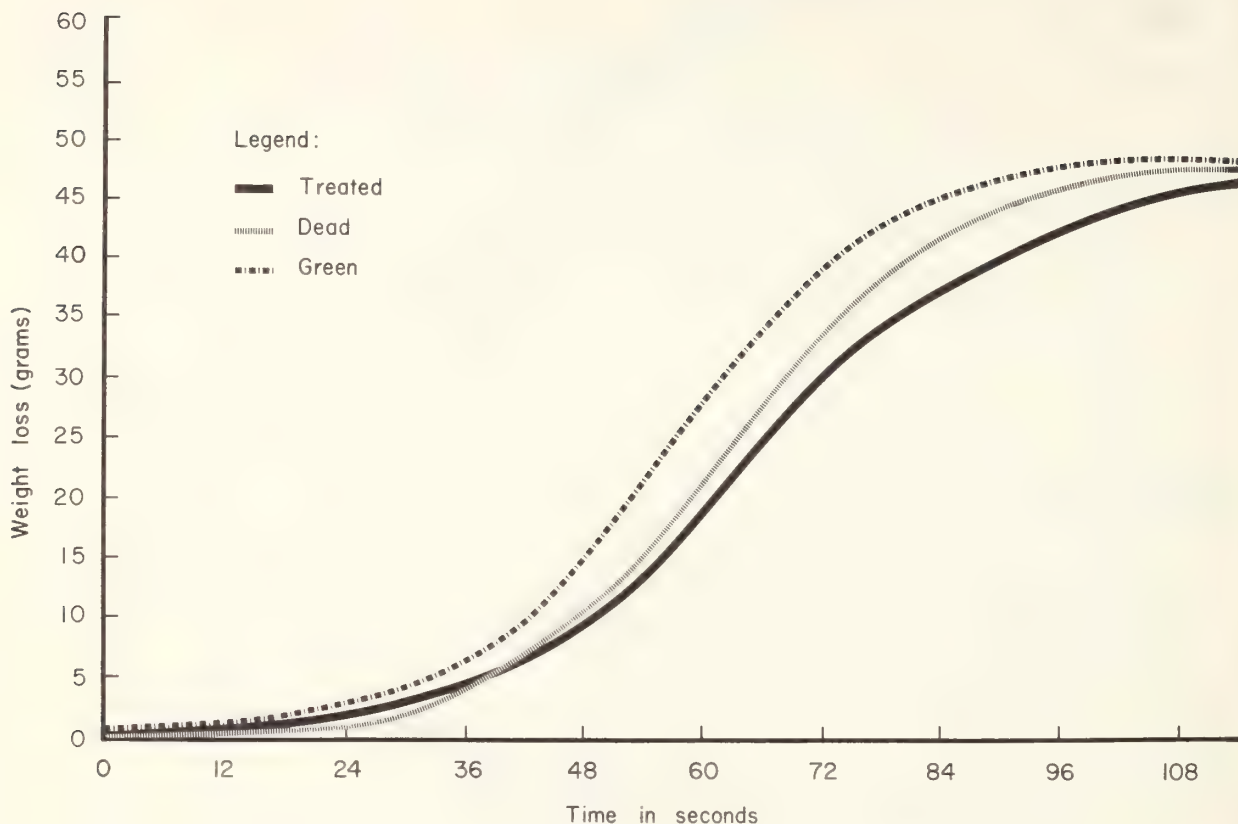


Figure 5. --The weight-loss curve for the small-scale burning tests.

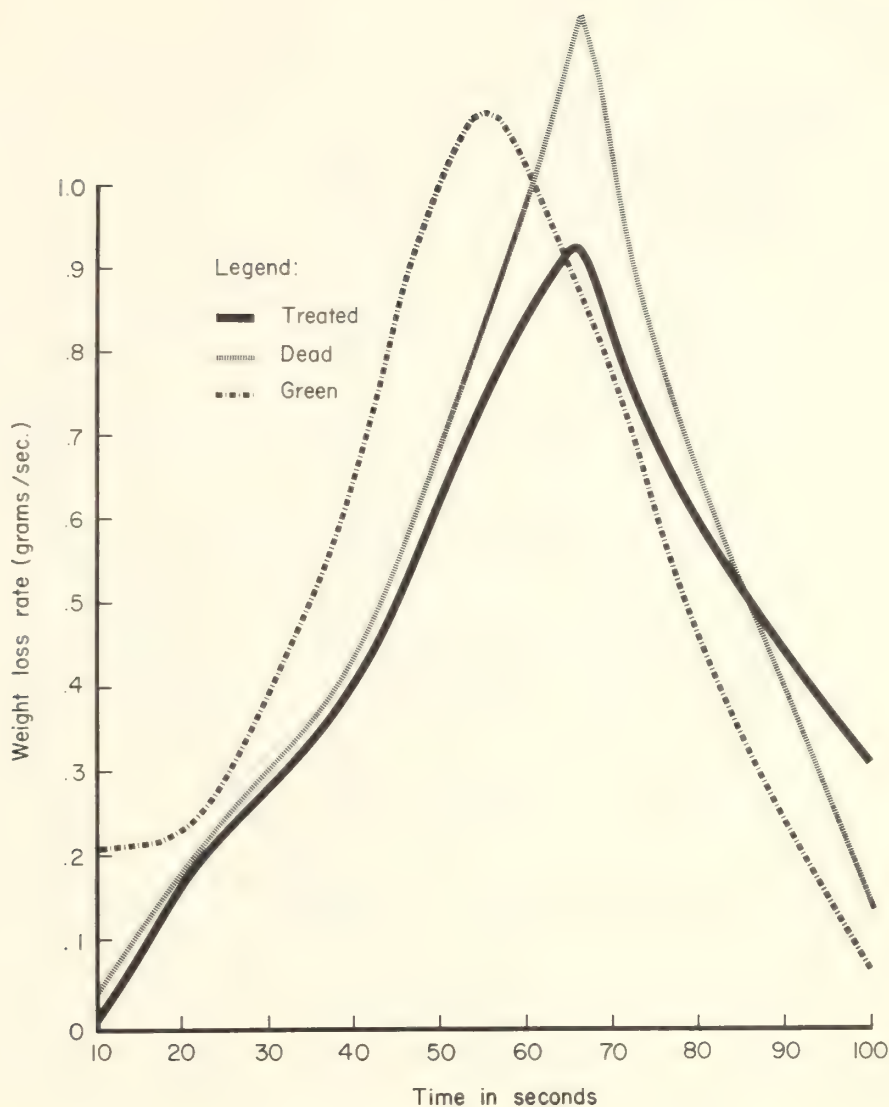
High ash content of the treated leaves corresponded with a decrease in the pyrolytic rate and an increase in residue, or a reduction in volatile production. The cellulose endotherm and exotherm in the DTA analysis were smallest for the treated leaves. Similar results are observed when pure cellulose is treated with inorganic contaminants (2). Apparently the cellulose in natural fuel responds to treatment in the same way as pure cellulose. However, in tests of the treated leaves, the temperatures at which pyrolysis occurred did not change with treatment as they did in tests of cellulose.

The results of the small-scale burning tests tended to agree with those of the TGA curves in N_2 and air. The maximum and average weight loss rates and energy release rates were lowest for treated foliage and highest for dead foliage. The differences between treatments seem to be greater in the burning tests. This could be due to the effects of the nonpyrolytic volatiles on the combustion rate. Extractives would have little effect on the TGA curves because they volatilize well below $200^\circ C$.

Conclusions

1. Herbicide-treated foliage of guava had a higher ash content and a lower ether-extractive content than green leaves or naturally killed leaves.

Figure 6.--The weight-loss rate for guava from the small-scale burning tests.



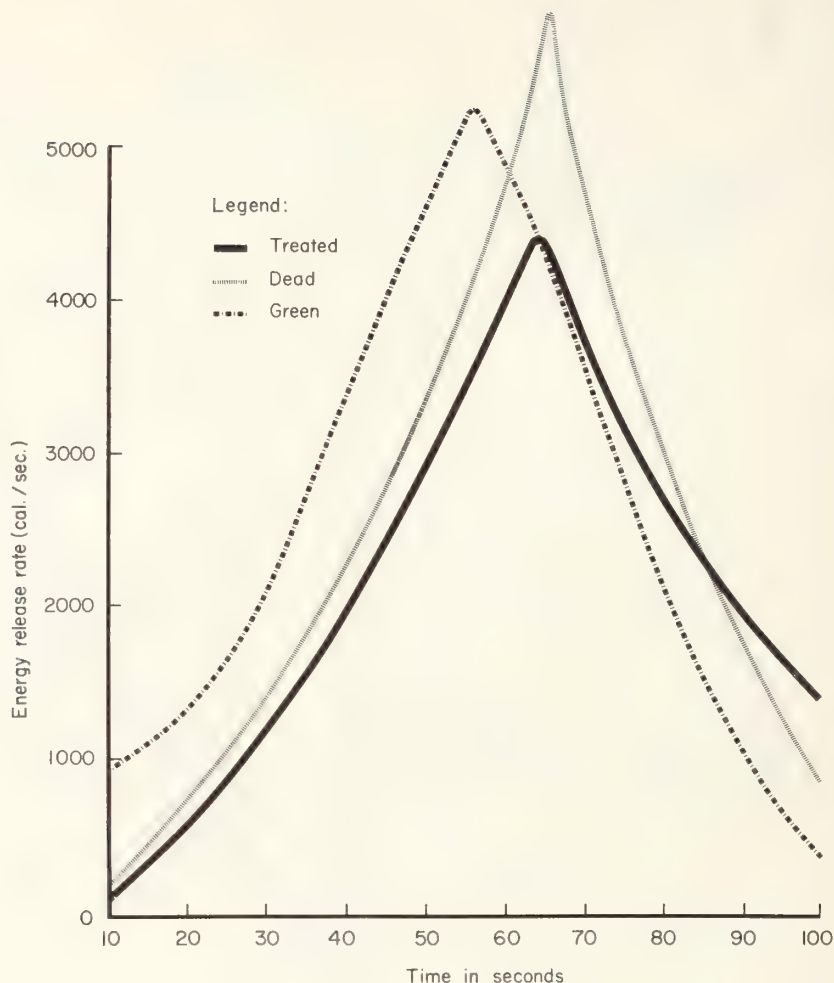
2. The higher ash content of treated leaves affected the TGA curves, reducing the weight-loss rate and increasing the residue at 450° C. This means less volatiles were produced by the treated fuels. The DTA of treated leaves showed a reduction in endotherm and exotherm intensity.

3. The increase in ash and/or the decrease in extractives reduces the burning rate of guava.

4. This study gives support to the possibility of using TGA to replace the more complicated and time-consuming burning tests.

5. Treatment of guava with 2,4-D and 2,4,5-T does not increase flammability with respect to naturally killed foliage, environmental conditions being equal. The herbicides kill the leaves and reduce their moisture content, making them more flammable than living leaves; however, no pyrolytic advantage is gained because of induced

Figure 7.--The energy-release rate for guava from the small-scale burning tests.



chemical changes. Guava is probably not highly flammable in the first place because of its high mineral content.⁴ The TGA residues, as compared to those of highly flammable species, substantiate this.

6. The herbicide probably increases the decomposition rate, leading to a higher ash content on a dry-weight basis because of the mass change. The extractives may be degraded by herbicidal treatment also.

⁴ Philpot, Charles W. Mineral content and pyrolysis of selected plant materials. U.S.D.A. Forest Serv., Intermountain Forest and Range Experiment Station. (In preparation.)

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